Five new homoleptic [NiX4]2− compounds have been prepared with the fluorinated ligands OC₆F₅ (OArF), OC₆H₃(CF₃)₂ (OAr′F), and OC₆F₅ (ORF) and characterized with X-ray crystallography, magnetic susceptibility, and elemental analysis. Electronic spectral studies show that these ligands engender a ligand-field environment similar to that of fluoride and thus act electronically like fluoride, but with none of the drawbacks of F− as a transition-metal ligand.

Homoleptic and mononuclear aryloxide complexes of the form [M(OAr)₄]m− or analogous alkoxides such as [M(OR)₄]m− have proven challenging to synthesize because of the propensity of these ligands to bridge multiple metal centers. Previous work demonstrated that extensive fluorination of aryloxide rings permits the isolation of homoleptic phenolate anions with CoII and CuII.1 Under analogous conditions with nonfluorinated phenolate, only low yields of dimeric structures are obtained.1 Herein we report the extension of this chemistry to NiII with two fluorinated aryloxides and one fluorinated alkoxide that has resulted in tetrahedral nickel anions surrounded by heavily fluorinated oxygen-donor ligands. UV−vis and near-IR spectroscopic analysis has been carried out to describe these newer ligands in the context of the traditional spectrochemical series.

The homoleptic anions with fluorinated aryloxides of the form [Co(OAr)₄]2− and [Cu(OAr)₄]2− were readily obtained by metathesis reactions of metal halides MX₂ with potassium or thallium salts of the appropriate aryloxide anion.1 Such reactions were unsuccessful in the case of nickel. With NiCl₂ or NiCl₂(DME), incomplete substitution was observed with either potassium or thallium aryloxide salts, and with Ni₂Cl₂ reduction to Ni0 occurred.

An alternative synthesis via the fluorinated phenols HOArF and HOAr′F succeeded. Alcoholysis of [CP₂Ni] with 2 equiv of phenol and 2 equiv of the appropriate aryloxide in tetrahydrofuran at reflux for several days was necessary. As shown in Scheme 1, potassium aryloxides and crown compounds were used to synthesize {K(18C₆)}₂[Ni(OArF)₄] (1), {K(benzo-18C₆)}₂[Ni(OAr')₄] (2), {K(18C₆)}₂[Ni(OAr'F)₄] (3), and thallium aryloxide, TIOAr′F, was used for the preparation of [Tl₂Ni(OAr′F)₄] (4). The formation of Ni−OAr linkages via alcoholysis is rare but not unprecedented. Previously, [CP₂Ni] had been reacted with phenols to make phosphine phenolate complexes,2,3 a bridging phosphate with pendant phenol,4 and an N-heterocyclic functionalized salen derivative.5 An earlier report was made of green material isolated from the reaction of TIOAr′F and NiCl₂ in CH₃CN characterized only as having the stoichiometry [Ni(OAr′F)₄]₂.6

Notably, the metathesis reaction of NiI₂ and 4 equiv of KOR′F works well for the alkoxide case [K(18C₆)]₂[Ni(OAr′F)₄] (5), as depicted in Scheme 2. This result suggests that the sensitivity

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Scheme 1. Synthesis of Fluorinated Homoleptic Nickel Aryloxide Complexes

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of Ni\textsubscript{2} to reduction, in the presence of aryloxide but not alkoxide ligands, may be due to the relative ease of oxidation of aryloxide anions versus alkoxide ones.

Repeated attempts to make 5 with 2 equiv of 18C6 were unsuccessful. Purple crystalline material that analyzed as 5 was obtained with some additional colorless material, probably 18C6. We hypothesize that the 3-fold coordination of the uncrowned K\textsuperscript{+} by the three CF\textsubscript{3} groups, vide infra, is more favorable than coordination by the crown ether.

All of the structures of the divalent nickelate complexes 1–5 are approximately tetrahedral at Ni\textsuperscript{II} with [NiO\textsubscript{4}] coordination, except in 4, where the coordinated Tl atoms create greater distortion. X-ray crystallographic studies were carried out according to the parameters collected in Table S1 of the Supporting Information. Only the connectivity of 1 was obtained from a low-quality data set, but the stoichiometry was confirmed.\textsuperscript{7} Within the limits of the data set, the structure of 1 is very similar to that of 2. The precise interatomic metrical parameters for 2–5 from the diffraction experiments are summarized in Table S2 of the Supporting Information. Only the connectivity of 1 is determined for comparison purposes, and an ORTEP is presented in Figure S1 of the Supporting Information.

The structure of compound 2 is tetrahedral at Ni with a dihedral angle between the O1–Ni–O2 and O3–Ni–O4 planes of 85.6°. On the left side of Figure 1, the cations and anion are shown, revealing that two O atoms are bridged by an encapsulated \{K(18C6)\}\textsuperscript{+} cation on each side of the complex. The average K–O\textsubscript{Ac} distance is 2.815(13) Å, which is longer than the K–O\textsubscript{Ac} bond distance of 2.6123(11) Å in 6. The weak interactions between K and the aryloxide O atoms cause the subtended O–Ni–O angles to be smaller [average = 89.0(5)°] than those without bridging K centers [average = 120(8)°]. The Ni–O distances exhibit a short (average = 1.934 Å) and long (average = 1.948 Å) distance in each pair bridged by a single K and are slightly longer than other Ni–O bond lengths in \{NiO\textsubscript{4}\} environments in the CSD,\textsuperscript{8} vide infra, because of the less basic O atoms. The OAr\textsuperscript{2} ligand has previously been bound as a terminal ligand to Ni in [(Ph\textsubscript{3}P)\textsubscript{2}Ni(OAr\textsubscript{2})\textsubscript{3}]\textsuperscript{+} and as a bridging ligand between two Ni centers in [(Ar\textsubscript{2}O\textsubscript{2}Ni(OtBu)\textsubscript{2}Ni(Ar\textsubscript{2}O\textsubscript{2})\textsubscript{2}]\textsuperscript{10} and \{[CpCo{P(=O)(OMe)}\textsubscript{2}]\textsubscript{2}Ni(OH\textsubscript{2})(H\textsubscript{2}OAr\textsubscript{2})\textsubscript{2}\}\textsuperscript{11}.

Compound 3, depicted in Figure S2 of the Supporting Information, is quite similar structurally to 2 with a slightly smaller dihedral angle of 82.4°. The Ni–OAr\textsuperscript{2} linkage has only been measured previously in [(Ph\textsubscript{3}P)\textsubscript{2}Ni(OAr\textsubscript{2})\textsubscript{3}] [Ni–O = 1.857(2) Å].\textsuperscript{9}

The unit cell of 4 has two independent \{Tl\textsubscript{2}Ni(OAr\textsubscript{2})\textsubscript{4}\} molecules, only one of which is shown in Figure S3 of the Supporting Information, with a \{Ni(OAr\textsubscript{2})\textsubscript{4}\}\textsuperscript{2–} core similar to that of 1 and 2, distorted somewhat by the bridging Tl atoms. The stoichiometry of 5 includes one \{K(18C6)\}\textsuperscript{+} cation and one crown-free K per Ni center. The crown-free coordination of K3 creates a pseudo-3-fold axis along the K3···Ni1 vector, as shown in Figure 2. The K3–Ni1–O4 angle is 165.44(9)°, while the other three K3–Ni1–Ox angles average 56.5(4)°. In the crystal structure, there are three different K\textsuperscript{+} environments, as shown in Figure S4 of the Supporting Information. One \{K(18C6)\}\textsuperscript{+} unit, containing K2, bridges two \{Ni(OAr\textsubscript{2})\}\textsuperscript{2–} anions via two bridging fluoride atoms F31. Another \{K(18C6)\}\textsuperscript{+} unit containing K1 is not closely bound to any other moiety in the crystal lattice. The two remaining K\textsuperscript{+} ions, K3, are coordinated by three O atoms, O1–O3, from the alkoxide ligands and six F atoms from adjacent perfluoro-\textsubscript{-}\textsuperscript{ tert}-butyl groups, shown on the right side of Figure S4 of the Supporting Information. There are no previous reports of compounds containing the NiOAr\textsuperscript{2} unit.

There are only a few other examples of structurally characterized \{NiO\textsubscript{4}\} coordination in the literature, and all contain Ni\textsuperscript{II} that is part of one or more chelate rings, with an average Ni–O bond distance in the CSD of 1.87(7) Å. The majority of the examples are derivatives of nickel.

(7) P1, a = 13.383(6) Å, b = 13.508(6) Å, c = 18.540(8) Å, α = 82.676(6)°, β = 81.787(6)°, γ = 73.522(6)°.
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bis(acetylacetonate),\textsuperscript{12–19} some bis(o-catecholate) compounds,\textsuperscript{20,21} a few bimetallic species with bridging alko
dies,\textsuperscript{22–25} two salicyaldehyde complexes,\textsuperscript{26,27} two bridging aryloxides,\textsuperscript{28,29} and one polyoxometallate,\textsuperscript{30} complex.

Previously studied (pseudo)halogen [NiX\textsubscript{4}]\textsuperscript{2–} complexes with \( D_{\text{sd}} \) symmetry have magnetic moments in the range 3.5–4.0 \( \mu_B \). The compounds 1–5 are paramagnetic, with an average \( \mu_{\text{eff}} \) of 3.51 \( \mu_B \) for the \( \text{K}_{2}\text{NiX}_{4} \) species, as determined by Evans’ method at room temperature.\textsuperscript{31,32} These values are closest to that for [NiI\textsubscript{4}]\textsuperscript{2–}, 3.49 \( \mu_B \) and, in combination with UV–vis data, suggest that the fluorinated aryloxide and alkoxide ligands are among the stronger ligands in the “weak-field” manifold. Figgis has termed these ligands “medium field”\textsuperscript{33} in which there is more spin–orbit coupling, and more free-ion-like behavior, consistent with the Racah parameters obtained experimentally, vide infra.

The UV–vis–near-IR spectra of compounds 2–5 as well as that of [NiCl\textsubscript{4}]\textsuperscript{2–} are shown in Figure 3, and their absorption energies are compared with previously published data according to the method of Lever\textsuperscript{34,35} to obtain values for the Racah parameter \( B \) and the ligand-field parameter \( D_{\text{q}} \). All four spectra of the nickel complexes with fluorinated ligands show significantly blue-shifted spectra, compared to [NiCl\textsubscript{4}]\textsuperscript{2–}, indicating a stronger ligand field. The strongly electron-withdrawing and reduced \( \sigma \)-basic character of the ligands results in a large ligand-field splitting, as described by \( D_{\text{q}} \). The large Racah parameter \( B \) for 5 indicates strong interelectronic repulsion and primarily \( \sigma \)-donor character of the ligand. On the basis of these data, we write the following abbreviated spectrochemical series:

\[
\text{Br} < \text{Cl} < \text{NCO} \ll \text{ORF}^+ < \text{OArF}^- < \text{OR}^-
\]

These data demonstrate that the fluorinated aryloxide and alkoxide ligands are as strong in ligand-field terms as fluoride. Unlike fluoride, however, these ligands are much less prone to bridging, as complexes 1–3 and 5 attest. Thus, these ligands serve as an electronic equivalent of fluoride and are therefore expected to stabilize oxidation states for Ni higher than Ni\textsuperscript{2+}. A cyclic voltammogram (CV) of 5 with \( E_{\text{ox}} \) of \(-0.2 \text{ V vs Ag/Ag}^+ \) is shown in Figure S5 of the Supporting Information.

In summary, several new homoleptic tetrahedral nickelate complexes [Ni(OAr\textsubscript{F})\textsubscript{4}]\textsuperscript{2–} and [Ni(OR\textsubscript{F})\textsubscript{4}]\textsuperscript{2–} with extensively fluorinated aryloxide and alkoxide ligands have been prepared. Ligand-field studies show that these ligands are best described as “medium-field” and therefore are well positioned to stabilize high-oxidation-state molecules for potential use in C–H activation chemistry because of the ligand field generated and the highly oxidation-resistant ligands themselves.

Acknowledgment. We thank Boston University, NSF CAREER (Grant CHE-0134817), and ACS-PRF AC-4802 for financial support.

Supporting Information Available: Full experimental details, tabulated X-ray crystallographic information (Tables S1 and S2) for compounds 2–6, ORTEPs for compounds 3–6 (Figures S1–S4), a CV of 5 (Figure S5), and time-of-flight electrospray ionization mass spectrometry analysis of 4 (Figure S6). This material is available free of charge via the Internet at http://pubs.acs.org.

\textsuperscript{IC9003593}

Table 1. Electronic Spectral Data and Ligand-Field Parameters

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<th>[NiX\textsubscript{4}]\textsuperscript{2–}</th>
<th>( E(v_1) ) (cm\textsuperscript{-1})</th>
<th>( E(v_2) ) (cm\textsuperscript{-1})</th>
<th>( B ) (cm\textsuperscript{-1})</th>
<th>( D_{\text{q}} ) (cm\textsuperscript{-1})</th>
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Figure 3. UV-vis–near-IR spectra of [NiX\textsubscript{4}]\textsuperscript{2–} species.


